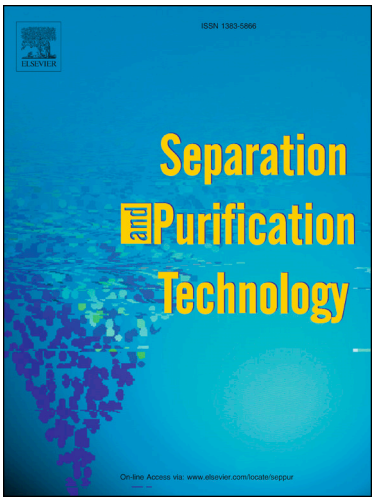


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PII: S1383-5866(17)31654-4
DOI: https://doi.org/10.1016/j.seppur.2017.12.057
Reference: SEPPUR 14290

To appear in: *Separation and Purification Technology*

Received Date: 11 May 2017
Revised Date: 27 December 2017
Accepted Date: 28 December 2017

Please cite this article as: R. Abejón, M.P. Belleville, J. Sanchez-Marcano, A. Garea, A. Irabien, Optimal Design Of Industrial Scale Continuous Process For Fractionation By Membrane Technologies Of Protein Hydrolysate Derived From Fish Wastes, *Separation and Purification Technology* (2017), doi: https://doi.org/10.1016/j.seppur.2017.12.057

# OPTIMAL DESIGN OF INDUSTRIAL SCALE CONTINUOUS PROCESS FOR FRACTIONATION BY MEMBRANE TECHNOLOGIES OF PROTEIN HYDROLYSATE DERIVED FROM FISH WASTES

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Highlights

- Fractionation process by UF and NF membrane cascades of a fish protein hydrolysate
- Basic integrated cascade identified as the most convenient configuration
- Freshwater consumption was avoided by implementation of water recovery and reuse system
- Product valued above the 95-212 $/m$^3$ range compensate the costs of the fractionation process

**Abstract**
The fractionation in an industrial-scale continuous process of a protein hydrolysate obtained from tuna wastes has been proposed. A model based on membrane transport equations, mass balances and economic equations to calculate the main costs of the process was developed. This model was applied to the evaluation of the main technical, environmental and economic aspects of the process and their optimization. The basic cascade configuration resulted better than alternative options like the linear or dual cascades. The freshwater consumption was minimized to improve the environmental and economic performance of the process. Indeed, the implementation of a water recovery and reuse system was the most effective solution. This system was based on the installation of an additional tight nanofiltration stage that reduced the environmental impact of the process (avoiding the need of auxiliary freshwater streams) and increased its economic competitiveness.

**Keywords:** Fish protein hydrolysate, Ultrafiltration, Nanofiltration, Fractionation process, Membrane cascades

## 1. Introduction

Both the extractive fishing (the harvesting of wild seafood) and the aquaculture (the cultivation of seafood) require posterior fish processing. The term fish processing refers to the processes associated with seafood products from the moment fish and shellfish are extracted from water to the moment the final products are delivered to the customers. Fish processing wastes can be defined as the fish material left over from primary processing during the fish manufacturing processes and include large quantities of substandard muscles, viscera, heads, skins, fins, frames, trimmings, and shell wastes [1]. These wastes account generally for a range from 30 to 50% of the total weight of the starting material [2].

The management of the wastes generated by fish processing industry poses environmental, economic, and logistic problems. Until recent times, these wastes have been discarded to landfilling or only used for very low value-added purposes, such as organic soil amendments. Nevertheless, novel alternatives have been developed to transform these undervalued wastes into more valuable by-products (Figure 1). Fish wastes can be seen as a resource to be used for energy generation. Although waste fish oil can be directly employed as combustible in boilers or furnaces, it results in

large particulate emissions and carbon deposits, so the proper conversion to a more suitable biofuel as biodiesel has been suggested [3,4]. Other fish processing wastes can be used as an energy-rich substrate for biogas production [5,6].

Figure 1

Nevertheless, fish wastes contain valuable substances for other segments of the food industry and different industrial sectors (mainly related to health and care). Although fish wastes are a significant source of polyunsaturated fatty acids, phospholipids, soluble vitamins or other bioactive compounds, the most remarkable resources to be recovered from fish wastes are valuable proteins and essential amino acids [7]. This remaining protein content in fish wastes can be used as raw material to obtain higher value-added products. The production of bioactive peptides from protein-rich fish wastes by hydrolysis has been intensely studied [8,9]. Fish protein hydrolysates are defined as the products from the chemical (using acid or alkali) or enzymatic hydrolysis reaction of peptide bonds in fish proteins, which result in shorter peptides or amino acids [10]. This modification improves the functional properties of native proteins and their usefulness as intermediate ingredients in the food, cosmetics, nutraceutical, and pharmaceutical industrial sectors.

The bioactive peptides present in fish protein hydrolysates exhibit potential for application as nutrition and health promoting agents [11]. Besides being relevant sources of nitrogen, which can be useful for improved animal and human nutrition [12], these biomolecules have diverse physiological functions within the body, including antioxidant, anti-inflammatory, immunomodulatory, hypolipidemic, hypocholesterolemic or antihypertensive properties [13]. Moreover, several bioactive peptides have demonstrated their multifunctional properties, including cancer preventive activity [14].

Enzymatic hydrolysis of proteins normally results in a very complex mixture of numerous peptides with different amino acid sequences and molecular weights from 0.4 to higher than 10 kDa. Fractions with molecular weight between 1 and 4 kDa have been identified as the most promising option for higher value-added value nutritional and pharmaceutical purposes [15,16]. Consequently, properly selected and designed separation techniques have to be developed to carry out the effective fractionation of the protein fractions.

Membrane technologies have been successfully implemented in efficient and ecological processes for the extraction (including concentration, purification and fractionation) of valuable biomolecules from waste streams. For the particular case of protein hydrolysates, ultrafiltration (UF) and nanofiltration (NF) can be applied to separate peptides based on their size, charge and hydrophobicity characteristics. The applicability of ultrafiltration and nanofiltration to separation tasks for fish protein hydrolysates has been investigated [17-23].

Advanced membrane configurations, such as membrane cascades, have been successfully applied to the integration of several separation stages in order to overcome the constraints of limited membrane selectivity and improve the effectiveness of the separation processes [24,25]. Recent efforts have been focused on the in-silico evaluation of ultrafiltration and nanofiltration membrane cascades for fish protein hydrolysate [26].

Taking into account the analysis of the results presented by previous works related to membrane cascades for protein hydrolysate fractionation, new efforts were required to investigate the implementation of this type of process in real industrial-scale installations. Therefore, the objective of this work was to study the fractionation process at ~~on~~ the industrial scale, considering two main issues. On the one hand, the design of different alternative configurations of the membrane cascades was carried out to find the optimal technical solution. On the other hand, the implementation of an optimal water auxiliary system was investigated, including the consideration of water recovery and reuse within the process. Lastly, the minimization of the total costs of the fractionation process was proposed. As a result, the definitive scaled-up process was subject to optimization taking into account the most relevant technical, environmental and economic aspects.

## 2. Case study

Fish canning industry is a very important sector in the Spanish food productive system: it markets more than 260,000 ton annually. Tuna must be highlighted as the most consumed canned fish product, as it reaches 55% of the total consumption [27]. This trend is similar in other countries over the world. The importance of tuna to world fish supply has to be remarked: the total amount of global tuna (and related species like bonitos and billfishes) catches is above 7 million tons per year [28]. Tuna processing industry generates large amount of solid wastes and even the most efficient canning installations cannot attain yields higher than 55% [29,30]. Consequently, approximately half of the raw material becomes waste during tuna processing, so it appears as a suitable scenario to implement protein hydrolysis in order to obtain valuable by-products from fish solid wastes.

The design of the proposed industrial-scale installation for tuna processing fixed the plant capacity at 10,000 ton/y of raw material as intake. This figure fell in the upper zone of the range defined by typical sizes of fish processing plants [31,32]. Taking into account that 46% can be considered as an acceptable yield value for tuna processing, the total amount of fish wastes available for hydrolysis was 5,400 ton/y. Although the enzymatic hydrolysis conditions (hydrolysis time, temperature, pH, enzyme/solid ratio, liquid/solid ratio...) varied considerably among the different published references, the conditions defined in a previous collaborative research between the Institut Européen des Membranes in Montpellier (France) and the Laboratory of Materials Science and Environment of the Faculty of Science of Sfax (Tunisia) were selected [33]. The most determining condition for the plant dimensioning was the liquid/solid ratio, which defined the amount of clarified hydrolysate. The selected

2/1 ratio can be found in other references as a practical value [34,35]. Under consideration of continuous production for 300 days per year, the hydrolysis system resulted in 1.5 $m^3$/h of clarified hydrolysate with the composition shown in Table 1. The medium protein fraction (1-4 kDa) was the preferred one for nutraceutical and pharmaceutical applications, so the fractionation process was designed to improve the purity of this fraction in the product stream.

Table 1

**3. Process modeling**

The simulation model developed for the representation of the fractionation process by ultrafiltration and nanofiltration membranes has been previously published [26], based on the results of previous experimental works [36,37]. Simple models were proposed to describe the influence of the applied pressure on the permeation of the membranes and the rejection of each defined protein fraction [38]. Besides, the two main characteristics of the permeate streams, the flowrate and the corresponding protein fraction concentrations, were calculated taking into account the membrane area of the corresponding stage. Finally, the recovery ratio of each module Rec was expressed as the ratio between the flows of permeate and feed streams.

The performance of the fractionation cascades was described by the definition of two useful parameters. The first one was the purity of the product stream, measured as the percentage of the medium protein fraction over the total protein concentration:

$$X^{M} = 100 \frac{M^{M}_{MPROD}}{[TP]_{MPROD}} \quad (1)$$

The second parameter was the process yield, defined as the percentage of the medium protein fraction entering the system in the feed stream that was recovered in the product stream:

$$Y^{M} = 100 \frac{F_{MPROD} \cdot M^{M}_{MPROD}}{F_{FEED} \cdot M^{M}_{FEED}} \quad (2)$$

This technical model was complemented with economic considerations that consider the main costs of the system. The total daily costs of the system were calculated as the sum of the capital costs (CC) and the operation costs (OC):

$$TC = CC + OC \quad (3)$$

The CC attributable to membranes ($CC_{memb}$) or to the rest of the installation ($CCi_{nst}$) were differentiated:

$$CC = CC_{memb} + CC_{inst} \quad (4)$$

The membrane cascade can be divided into two sections: the ultrafiltration section and the nanofiltration section. The corresponding capital costs for each section were assessed independently because of their different characteristics. The capital cost of the membranes modules considering straight-line depreciation was expressed as function of the total membrane area of the installation:

$$CC_{memb} = CC_{membUF} + CC_{membNF} \quad (5)$$

$$CC_{membUF} = \frac{Y_{membUF} \sum A_{UFk}}{LT_{membUF}} \quad (6)$$

$$CC_{membNF} = \frac{Y_{membNF} \sum A_{NFk}}{LT_{membNF}} \quad (7)$$

Once the membranes costs were defined, the capital costs corresponding to the rest of the installation were related to them by mean of a coefficient ($K_{memb}$) that expressed the contribution of the investment in membranes to the total capital costs.

$$CC_{inst} = CC_{instUF} + CC_{instNF} \quad (8)$$

$$CC_{instUF} = CC_{membUF} \frac{(1 - K_{memb})}{K_{memb}} \frac{LT_{membUF}}{LT_{inst}} \quad (9)$$

$$CC_{instNF} = CC_{membNF} \frac{(1 - K_{memb})}{K_{memb}} \frac{LT_{membNF}}{LT_{inst}} \quad (10)$$

The OC were itemized into freshwater ($OC_{water}$), energy ($OC_{en}$), membrane cleaning ($OC_{clean}$), labor ($OC_{lab}$), and maintenance costs ($OC_m$):

$$OC = OC_{water} + OC_{en} + OC_{clean} + OC_{lab} + OC_m \quad (11)$$

The freshwater cost was based on the total consumption and the unitary price and, equivalently, the energy cost was based on the total electricity consumed to pressurize the feed streams of the membranes modules and the price of electricity:

$$OC_{water} = Y_{water} \sum Q_{water} \quad (12)$$

$$OC_{en} = \frac{\sum (F_{UPk} \Delta P_k)}{36\eta} Y_{elec} \quad (13)$$

The membrane cleaning cost considered a correction factor to take into account the influence of the total protein content of the stream feeding each membrane module. A linear relationship between the fouling potential of a stream and the corresponding membrane cleaning costs has been identified [39]:

$$OC_{clean} = Y_{clean} \sum \left( F_{UPk} \frac{[TP]_{UPk}}{[TP]_{REF}} \right) \quad (14)$$

Finally, the labor costs were attributed to the salaries paid to the operators and the maintenance costs were estimated as a function of the total capital costs:

$$OC_{lab} = 24 n_{lab} Y_{lab} \quad (15)$$

$$OC_{m} = 0.05 CC \quad (16)$$

The main technical and economic parameters required by the model are listed in Table 2.

Table 2

## 4. Results and discussion

### *4.1. Analysis of alternative cascade configurations*

The simulation of the fractionation process based on the integration of 3 UF stages and 3 NF stages under a basic cascade configuration was performed in a previous study [26]. Moreover, this previous study analyzed the influence of the main design decisions and operation conditions on the performance of the cascade. It revealed that high recovery rates in the membrane modules and low applied pressures were preferred to obtain maximal product purity.

Nevertheless, this previous work did not consider the implementation of alternative configurations for the fractionation process. The recirculation and integration of streams within a membrane cascade configuration can modify the performance of a separation process. Different cascade configurations must be designed depending on the type of separation that is required. Complex superstructures are able to encompass all the possible combinations of stripping and rectifying sections of solute fractionation cascades [40]. However, in this work, the superstructure was simplified to take into consideration only two predetermined configurations. The linear countercurrent integrated cascade [41] and the dual cascade [42] were selected as predetermined configurations because of their easier applicability.

Figure 2 compiles the 3 selected designs to be compared: the basic, linear and dual cascades. In this case, the configurations are depicted for the UF section, but the equivalent cascades for the NF section can be easily represented after replacement of the heavy stream by the medium stream and

the stream to NF section by the light stream. Due to the reduced number of configurations to be analyzed, the employment of a simulation software like Aspen Custom Modeler was preferred over the use of optimization tools. The fixed values of the recovery rates in the membrane stages were 0.9 and the applied pressures were 2 and 5 bar, for the UF and NF modules respectively. The flowrates of the water inlet streams (which are required to avoid excessive total protein content in the inlet streams) were equal to the flowrate of the feed stream of clarified hydrolysate (1.5 $m^3$/h) as described in the Case Study section above.

Figure 2

The main results obtained for the analysis of the influence of the cascade configuration on the performance of the UF section are compiled in Table 3. As it can be observed, the basic configuration was clearly the most advantageous one: it combined the highest fraction purity (21.1%) with the highest yield (93.8%). Moreover, the dual configuration was the least competitive, presenting the lowest values of purity (18.6%) and yield (69.8%). Taking into account that the initial purity in the feed stream was 19.0%, the dual configuration resulted in a lower value. This fact is due to the enrichment of the stream to be treated by NF in the light and ultralight fractions, as the comparison of the $X^M/X^L$ ratios demonstrated: 0.54 for the dual cascade against 0.64 for the basic configurations. However, the dual cascade was very effective for the removal of the heavy fraction. This configuration showed the lowest concentration of the heavy fraction in the stream to NF and, consequently, the highest value of the $X^M/X^H$ ratio. The basic cascade was the best alternative according to all the investigated parameters except this latter $X^M/X^H$ ratio, as its value was even below the one obtained by the linear configuration, which showed intermediate values for all the analyzed parameters.

Table 3

After the analysis of the obtained results (and more specifically, the relative ratios of the different protein ratios), the study continued with the consideration of the streams derived from the 3 alternative UF configurations as possible feed streams of the NF section. Although the basic UF configuration appeared as the most promising option, the consequences of different configurations were more deeply investigated. The most significant results of the process after the coupling of the UF and NF sections are included in Table 4.

Table 4

The highest product purity was obtained when the linear configuration in the UF section and the basic configuration in the NF section were integrated. The resulted value (49.5%) was just a bit higher than the value when basic configurations were implemented in both sections (49.3%). Nevertheless, this increased purity was attained at the expense of lower process yield: 58.6% versus 62.5%. Moreover, the corresponding $X^M/X^L$ ratio was slightly lower too (1.32 for the linear UF + basic NF cascade and

1.39 for the basic UF + basic NF cascade). Another very relevant aspect in the design of membrane cascades is the total membrane area required. This factor was selected to break the deadlock between both configurations, as one cascade needed considerably lower membrane area. While the linear UF section employed 277 $m^2$, the basic configuration was able to work just with 185 $m^2$, which implied a reduction around 33%. This aspect should be considered definitive to prefer the basic UF + basic NF cascade over the linear UF + basic NF one, despite the slightly higher purity that can be obtained by this last configuration.

Meanwhile, the dual configuration in the NF section appeared as a very valuable option to obtain very high values for the process yield. For example, when the basic UF + dual NF cascade was evaluated, the attained process yield was 91.8%. Taking into consideration that the yield of the basic UF section was 93.8%, these figures signified that the purity was increased from 21.1 to 33.1% with only a decrease in the yield around 2%. To get a better understanding of this fact, a basic UF + basic NF cascade optimally designed for maximal yield obtained a value of 91.9%, but the corresponding purity value was only 22.5% [26].

*4.2. Environmental optimization: Fresh water consumption minimization*

The selected membrane cascade configuration considered the implementation of 5 fresh water streams, one before each membrane stage but the first NF stage (Stage 1B). The main objective of these streams was the control of the total protein content of the different streams in order to avoid problems caused by too viscous solutions (membrane irreversible fouling or even clogging). For the technical evaluation of the different cascade configurations in the previous section, the flowrates of all these water streams were defined to be equal to the flowrate of the feed stream (1.5 $m^3$/h). Under these conditions, the maximal total protein content was found in the retentate stream of the first UF stage (Stage 1A), with a value of 281g/L. However, the rest of the streams in the cascade showed total protein contents clearly lower than this value. Although a previous study investigated the influence of the individually adapted water stream flowrates to maintain the total protein contents below a predefined maximal limit that can assure the correct operation of the fractionation process [43], this research work proposed a further analysis of the fresh water consumption and its effects over the main aspects of the process. Moreover, the minimization of the total freshwater consumption was performed to reduce the environmental charges of the process.

GAMS was chosen as the optimization software to be used for the determination of the optimal cascade design to minimize the fresh water consumption. In mathematical terms (general form with all the terms of the equations or inequalities in the left side) the optimization model can be expressed as follows:

$$\min Z = f(x)$$
$$\text{s.t. } h(x) = 0$$
$$w(x) \leq 0$$
$$x \in \Re^n$$
$$x_L < x < x_U$$

being Z the total freshwater consumptions (expressed as the sum of the flowrates of the 5 streams), x the vector of independent variables (flowrates of the freshwater streams), h the vector of equality constraint functions (material balance equations and membrane transport equations) and w the vector of inequality constraint functions defining the maximal limit for the total protein content to avoid problems with the membranes and the minimal purity and yield requirements to be achieved.

Figure 3 shows the results of the minimal water consumption (with the corresponding break-down to represent the different water streams individually) as function of the defined maximal limit for the total protein content.

Figure 3

The results clearly showed the relevance of the optimal distribution of the total water flowrate among the different streams. While the uniform distribution of 7.5 $m^3$/h resulted in a maximal protein content of 281 g/L (results not shown), the optimized process demonstrated that less than 3.6 $m^3$/h were enough to maintain all the protein contents below 250 g/L when the water streams were optimally defined. As it can be expected, the imposition of a stricter protein content limit implied the need of higher freshwater flowrates, but even the limit of 150 g/L could be attained with less than 7.0 $m^3$/h, which was still below the initial value of 7.5 $m^3$/h. Moreover, the lowest considered limit (100 g/L) required the consumption of 11.2 $m^3$/h, value that represented an increase lower than 50% when compared to the baseline uniform distribution case.

A more detailed analysis of the individual water streams revealed than the inlet of the second NF stage (Stage 2B) required the highest flowrate for all the considered cases. Meanwhile, the third UF stage (Stage 3A) was the one with the lowest flowrate until the limit of 175 g/L was attained, as the limits higher than this value resulted in the first UF stage (Stage 1A) as the minimal. The case of this last stream was very particular. Although it operated with the minimal flowrate for limits above 175 g/L, this stream was the second most demanding one when 100 g/L was fixed as limit, very close to the Stage 2B flowrate (2.9 and 2.7 m3/h for Stage 2B and 1A respectively). This evolution from low water consumption with high limits to high consumption with low limits could be explained by the mixing of the Stage1A stream with the feed stream. While the protein content of the feed stream was constant, the protein contents of the rest of streams, and specifically, those ones to be mixed with the water inlets, were variable and influenced by the fixed limit. Consequently, the attainment of the protein content requirements for the Stage 1A was easier when high limits were imposed because it started from a constant value lower than the values corresponding to the rest of the streams. Therefore, the

distribution of the water among the different inlet streams was revealed as a very important aspect of the fractionation process in order to minimize the total water consumption without the appearance of problems in the installations because of excessive protein contents.

Another important aspect to be considered during the minimization of the water consumption in the fractionation process was the analysis of the effects over the total membrane area required in the system. It could seem obvious that minimal water flowrates entering the installation implied lower membrane area. However, this was not the case. As an illustrating example, when the baseline case with uniform distribution and total flowrate of 7.5 $m^3$/h was compared in terms of total membrane area to the optimal cascade for 250 g/L as limit, the results showed an increase in the membrane area higher than 11% (776 and 695 $m^2$ respectively), while the total water consumption was reduced 52%. This increase was mainly due to the higher membrane area required in the NF section, since the membrane areas in the UF section were very similar in both cases.

The analysis of the influence of the limit for the total protein content on the required membrane area helped to understand the reason for these additional needs. As it can be observed in Figure 4, the relationships between the defined limits and the membrane areas were not so simple and followed complex trends. On the one hand, the UF section showed an asymptotic behavior since the membrane areas reached constant values for limit values above 200 g/L. On the other hand, in the NF section minimal membrane areas could be identified: they corresponded with 150 g/L for the second and third stages (Stages 2B y 3B) and with 200 g/L for the first stage (Stage 1B). These results can be explained by the influence of the total protein content on the permeability of the membranes. For the case of the UF membrane, the reduction of its permeability at high protein contents was just balanced with the reduced flowrate of permeate to be recovered with low water inlets. This way, the membrane area remained almost constant once a determined protein content limit was exceeded. However, this is not the case of the NF membrane. Its permeability was more intensively reduced for higher protein contents. Consequently, the expected reduction of the membrane area due to the reduced flowrate of water was not able to compensate the higher additional membrane area required to counteract the decreased membrane permeability.

Figure 4

4.3. *Economic optimization: Cost minimization*

As demonstrated in the previous section, taking the complex relationship between the total freshwater consumption and the total membrane area as example, different environmental criteria (minimal freshwater consumption or minimal membrane area requirements) may be exclusive and multi-objective optimization can be proposed to clearly identify the correlations among the different criteria. In this case, the economic optimization of the membrane cascade has been considered as a valuable

tool to identify the economic consequences of the environmental aspects of the system. Despite the fact that previous work has been carried out to investigate the economic aspects of fractionation processes by membrane cascades [43], this work carried out further analysis to take into consideration the economic aspects of a real industrial-scale fractionation process. The minimization of the total costs of the fractionation process was carried out for different total protein content limits using GAMS. In mathematical terms, the optimization model can be expressed as follows:

$$\min Z' = f(x)$$
$$\text{s.t. } h(x) = 0$$
$$w(x) \leq 0$$
$$x \in \Re^n$$
$$x_L < x < x_U$$

being Z´ the total costs of the process, x the vector of independent variables (flowrates of the freshwater streams), h the vector of equality constraint functions (material balance equations and membrane transport equations, as well as economic model equations) and w the vector of inequality constraint functions defining the maximal limit for the total protein content to avoid problems with the membranes and the minimal purity and yield requirements to be achieved.

The results obtained can be seen in Table 5. According to the optimization results, it was clear that the minimization of the total freshwater consumption had greater economic influence over the total costs of the system than the total membrane area minimization. Minimal total costs were obtained for minimal freshwater consumption for all the defined total protein content limits. Operation costs were higher than capital costs and the freshwater costs were the main component of the operation costs for protein content limits below 200 g/L. For values greater than 200 g/L, the freshwater consumption was less significant and the labor costs became predominant. While the contribution of freshwater costs to the total costs were ranged between 27 and 52%, the contribution of the membrane costs were not higher than 9% for all the analyzed cases. The analysis of membrane costs revealed that its minimal value corresponded to 200 g/L. However, the minimal UF membrane costs corresponded to 225 g/L and the minimal NF membrane costs to 175 g/L, but the case defined by a fixed limit of 200 g/L represented the best balance between both sections of the fractionation process.

Table 5

Moreover, the economic optimization of the process was useful to investigate the potential profitability of the fraction process by membrane cascade. Once the total costs of the process were assessed, it was possible to estimate the required revenues to obtain a profitable process. Therefore, the calculation of the minimal assignable value Z, that is, the minimal economic value the product stream must have to compensate the total costs of the system, was proposed.

The Table 6 complies the different flowrates and characteristics of the product streams and the calculated assignable value. As it can be observed, the values felt into the range between 188 (for the

most diluted case with protein content limited to 100 g/L) and 285 $/m$^3$ (for the most concentrated case with protein content limited to 250 g/L). It must be highlighted that the two sub-product streams (light and heavy streams) were not considered for the economic evaluation, although it was clear that both streams had valuable characteristics and they can contribute to increase the revenues of the fractionation process.

Table 6

4.4. *Improvements in environmental and economic aspects by implementation of water recovery and reuse system*

The economic analysis of the process has revealed the high relevance of the freshwater consumption over the total costs of the fractionation cascade. Most part of the consumed water left the cascade in the light stream, which was characterized by a high flowrate and dilute protein concentrations. Water usage efficiency can be clearly improved by increasing water recovery and reuse rates. By coupling the membrane cascade to an additional water recovery membrane stage, the entire fractionation process could proceed automatically in a closed-loop configuration (without the need of supplementary freshwater inlet streams), as previously proposed for organic solvent systems [42,44]. The scheme of the cascade that resulted after the implementation of the water recovery and reuse system is depicted in Figure 5.

Figure 5

The additional water recovery stage (Stage 1C) was based on the use of a tight NF membrane. These membranes have demonstrated their potential for almost total rejection of low molecular weight organic compounds while maintained a high permeate flowrate and showed better pressure resistance (higher applied pressures can be considered). In this work, the NF90 membrane by Dow Filmtec was selected. This membrane showed total rejection for organic compounds with molecular weights similar to the peptides of the protein hydrolysate, so it was considered totally impermeable to the different protein fractions [45]. The membrane permeability was 11.2 L/h·m² bar and the maximal allowed applied pressure was 8.2 bar (the water recovery stage was designed to work at this maximal applied pressure). Besides, its unitary price was considered to be equal to the other NF membrane employed in the cascade (50 $/m$^2$).

As a consequence of the total removal of protein fractions in the permeate stream of the water recovery stage, this stream could be directly recovered to replace the water inlet streams just by recirculating it back to the process. Moreover, a more concentrated light stream was obtained as by-product. The process including the water recovery and reuse stage was optimized to minimize the total amount of water to be recovered to maintain the protein total contents below the fixed limits. The

obtained results confirmed the viability of the proposed design. The total amount of water required to attain the imposed limits did not change when compared to the cascade without water recovery and the system was able to recover it from the light stream without any additional water inlet to the process. The required membrane area in the water recovery stage (Stage 1C) depended on the imposed upper content: from 39 $m^2$ for 250 g/L to 121 $m^2$ for 100 g/L. Nevertheless, in all the cases this membrane area was totally comparable to the dimension of the other NF stages incorporated in the cascade and it did not imply implementation problems. For instance, the membrane area in the first NF stage (Stage 1B), which is the stage with higher required membrane area, ranged from 246 to 297 $m^2$ for the same protein content limits.

The economic evaluation of the fractionation process with water recovery was completed. Two different scenarios were proposed: the minimization of the total costs of the fractionation process and the minimization of the total water amount to be recovered. The obtained resulted are compiled in Table 7.

Table 7

As it can observed, both scenarios coincided for protein content limits below for the lowest investigated cases (100 and 150 g/L), but they changed for the highest limits (200 and 250 g/L), although the differences were not too important. As previously identified during the analysis of the fractionation process without water recovery, the influence of the more concentrated streams on the permeability of the membranes in the NF section was very relevant. In this case, as the water recovery system eliminated the costs attributable to fresh water consumption, the costs related to the membranes became more relevant and they could not be compensated with the reduced water costs. Therefore, the minimization of the total costs of the process with water recovery resulted in minimization of membrane area instead of the minimization of water to be recovered.

Nevertheless, the reduction of the total costs of the system due to the implementation of the water recovery stage was clear. The total costs decreased from 712 to 531 \$/d for the case of 250 g/L as imposed limit (which implied a 25% reduction). However, the saving was much more important for the most exigent limit of 100 g/L: they decreased from 1174 to 596 \$/d (a 49% reduction). Under these new conditions, the process became more easily profitable as the assignable values to the product stream were also reduced. The new assignable values ranged from 95 \$/$m^3$ for 100 g/L to 212 \$/$m^3$ for 250 g/L. Therefore, the obtained results have demonstrated that the implementation of the water recovery system provided advantages in both environmental and economic aspects of the process. These new conditions implied the elimination of fresh water consumption, the reduction of the membrane area in the NF section and decreased total costs.

## 5. Conclusions

The fractionation process by UF and NF membrane cascades of a protein hydrolysate obtained from tuna processing by-products was scaled-up. The proposed simulation model was based on empirical equations for solvent and solute transport through the membranes and the corresponding mass balances for membrane modules and stream mixers. Besides, a simple economic model to assess the main costs of the process was developed.

The model was applied to the identification of the most convenient configuration among three different alternatives that integrate 3 UF stages and 3 NF stages: basic, linear and dual cascades. Although the maximal product purity (49.5%) was obtained when the linear configuration in the UF section and the basic configuration in the NF section were integrated, the implementation of the basic configuration in both section was preferred because the corresponding yield value (62.5% for the basic configuration against 58.6% for the linear configuration) compensated the little decrease resulted in the product purity (49.3%). Moreover, a 33% saving in the total membrane area of the UF section was achieved when the basic configuration was implemented in this section instead of the linear configuration. Meanwhile, the dual configuration in the NF section appeared as a very valuable option to obtain very high values for the process yield (when the basic UF + dual NF cascade was evaluated, the attained process yield was 91.8%).

Auxiliary freshwater streams were required to control the total protein content of the inlet and outlet streams in the membrane modules. This way, clogging problems can be avoided just maintaining the total protein content below defined limits. The process optimization to minimize the freshwater consumption was carried out. Nevertheless, the minimization of the total costs of the process was useful to assess the contribution of freshwater costs to the total costs and they were ranged between 27 and 52% depending on the fixed limit for the total protein content.

Therefore, the design of a water recovery and reuse system implied improvements in both environmental and economic aspects of the process. The implementation of an additional tight NF stage was able to eliminate the continuous consumption of freshwater. The corresponding total costs decreased between 25 and 49% and the process was more easily profitable, since the required product values to compensate the total costs of the fractionation process ranged from 95 $\$/m^3$ to 212 $\$/m^3$ for total protein limits of 100 and 250 g/l respectively.

**Acknowledgements**

This project has received financial support from the Spanish Ministry of Economy and Competitiveness (MINECO) through CTQ2014-56820-JIN Project, co-financed by FEDER funds.

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NOMENCLATURE

| | |
|---|---|
| $A_{MEMB}$ | Membrane area ($m^2$) |
| $A_{NFk}$ | Total NF membrane area in the k stage ($m^2$) |
| $A_{UFk}$ | Total UF membrane area in the k stage ($m^2$) |
| CC | Total capital costs ($/d) |
| $CC_{inst}$ | Capital costs attributable to the installation ($/d) |
| $CC_{instNF}$ | Capital costs attributable to the installation of the NF section ($/d) |
| $CC_{instUF}$ | Capital costs attributable to the installation of the UF section ($/d) |
| $CC_{memb}$ | Capital costs attributable to the membranes ($/d) |
| $CC_{membNF}$ | Capital costs attributable to the membranes of the NF section ($/d) |
| $CC_{membUF}$ | Capital costs attributable to the membranes of the UF section ($/d) |
| $F_j$ | Flow rate in j stream ($m^3$/h) |
| $J_P$ | Permeate flux (m/h) |
| $K_{memb}$ | Ratio membrane capital costs to total capital costs (-) |
| $K_R$ | Filtration resistance constant ($m \cdot L^{0.5}/h \cdot bar \cdot g^{0.5}$) |
| $L_{P0}$ | Baseline membrane permeability (m/h·bar) |
| $LT_{inst}$ | Installation lifetime (d) |
| $LT_{membNF}$ | NF membrane lifetime (d) |
| $LT_{membUF}$ | UF membrane lifetime (d) |
| $M_j^i$ | Concentration of the i protein fraction in the j stream (g/L) |
| $n_{lab}$ | Number of workers assigned to the process ($/h) |
| OC | Operation costs ($/d) |
| $OC_{clean}$ | Operation costs due to membrane cleaning ($/d) |
| $OC_{en}$ | Operation costs due to energy consumption ($/d) |
| $OC_{lab}$ | Operation costs due to labor costs ($/d) |
| $OC_m$ | Operation costs due to maintenance ($/d) |
| $OC_{water}$ | Operation costs due to freshwater consumption ($/d) |
| Q | Flow rate of the stream leaving the UF section to enter the NF section ($m^3$/h) |
| $Q_{WATER}$ | Flow rate of the freshwater streams ($m^3$/h) |
| $R^i$ | Rejection of the i protein fraction (-) |
| Rec | Recovery rate (-) |
| TC | Total costs ($/d) |
| $[TP]_j$ | Total protein content in the j stream (g/L) |
| $[TP]_{REF}$ | Total protein content defined as baseline for membrane cleaning cost estimation (g/L) |
| $X^i$ | Purity of the i protein fraction (%) |
| $Y^i$ | Process yield for the recovery of the i protein fraction (%) |
| $Y_{clean}$ | Membrane cleaning unitary cost ($/$m^3$) |
| $Y_{en}$ | Electricity price ($/kWh) |
| $Y_{lab}$ | Salary ($/h) |

| | |
|---|---|
| $Y_{membNF}$ | Price of the NF membrane ($/m$^2$) |
| $Y_{membUF}$ | Price of the UF membrane ($/m$^2$) |
| $Y_{water}$ | Freshwater price ($/m$^3$) |
| Z | Assigned value of the product stream ($/m$^3$) |

**Greek symbols**

| | |
|---|---|
| $\Delta P_k$ | Applied pressure in the k stage (bar) |
| $\eta$ | Pump efficiency (-) |

**Indexes**

| | |
|---|---|
| i | Protein fraction |
| j | Stream |
| k | Membrane stage |

**Superscripts (Protein fractions)**

| | |
|---|---|
| H | Heavy protein fraction |
| L | Light protein fraction |
| M | Medium protein fraction |
| UH | Ultrahigh protein fraction |
| UL | Ultralight protein fraction |

**Subscripts (Streams)**

| | |
|---|---|
| FEED | System feed stream |
| HPROD | Heavy by-product stream |
| LPROD | Light by-product stream |
| MPROD | Medium product stream |
| PERM | Module permeate stream |
| RET | Module retentate stream |
| UP | Module feed stream |

CAPTIONS

Table 1. Composition of the clarified protein hydrolysate from tuna processing wastes.

Table 2. Parameters for the economic model.

Table 3. Results of the analysis of the influence of the configuration in the UF section on the process performance.

Table 4. Results of the analysis of the influence of the configuration in the NF section on the process performance (consideration of the three different configurations in the UF section).

Table 5. Optimal economic results of the analysis of the influence of the maximal allowed total protein concentration.

Table 6. Influence of the maximal protein content imposed in the system on the minimal assignable value for the product stream in order to be a profitable process.

Table 7. Optimal results of the fractionation process including the water recovery system as functions of the maximal allowed total protein concentration.

Figure 1. Scheme of upgrading applications for fish processing wastes (Adapted from the publication by Pérez-Gálvez and Bergé [72]).

Figure 2. Scheme of the different cascade configurations selected for analysis: basic (A), dual (B) and linear countercurrent (C) configurations.

Figure 3. Influence of the maximal allowed total protein concentration on the total freshwater consumption and contribution of each membrane stage.

Figure 4. Membrane areas for each membrane stage in the ultrafiltration (a) and nanofiltration (b) sections as functions of the maximal allowed total protein concentration.

Figure 5. Scheme of a six-stage cascade (basic configuration in both sections) with water recovery stage.

Table 1

| Protein Fractions | Molecular weight range (kDa) | Concentration (g/L) | Composition (wt%) |
|---|---|---|---|
| Ultra-heavy (UH) | > 7.0 | 8.3 | 11.5 |
| Heavy (H) | 4.0 - 7.0 | 2.1 | 3.0 |
| Medium (M) | 1.0 - 4.0 | 13.7 | 19.0 |
| Light (L) | 0.3 - 1.0 | 20.5 | 28.5 |
| Ultra-light (UL) | < 0.3 | 27.4 | 38.0 |
| Total protein | | 72.0 | 100.0 |

Table 2

| Parameter | Unit | Value |
|---|---|---|
| $Y_{membUF}$ | ($/m$^2$) | 800 |
| $Y_{membNF}$ | ($/m$^2$) | 50 |
| $LT_{membUF}$ | (d) | 3650 |
| $LT_{membNF}$ | (d) | 1095 |
| $LT_{inst}$ | (d) | 5475 |
| $K_{memb}$ | | 0.25 |
| $Y_{water}$ | ($/m$^3$) | 2.29 |
| $Y_{clean}$ | ($/m$^3$) | 0.38 |
| $[TP]_{REF}$ | (g/L) | 50 |
| $Y_{lab}$ | ($/h) | 12 |
| $n_{lab}$ | | 1 |
| $Y_{elec}$ | ($/kWh) | 0.15 |
| $\eta$ | | 0.70 |

Table 3

| | Configurations | | |
|---|---|---|---|
| | **Basic** | **Linear** | **Dual** |
| $Y^M$ | 93.8 | 88.0 | 69.8 |
| $X^M$ | 21.1 | 20.4 | 18.6 |
| $X^H$ | 1.57 | 0.78 | 0.17 |
| $X^M / X^H$ | 13 | 26 | 111 |
| $X^L$ | 33.0 | 33.5 | 34.0 |
| $X^M / X^L$ | 0.64 | 0.61 | 0.54 |
| **To NF section** | | | |
| Q ($m^3/h$) | 4.334 | 4.313 | 4.313 |
| $M^M$ (g/L) | 4.44 | 4.19 | 3.32 |
| $M^H$ (g/L) | 0.33 | 0.16 | 0.03 |
| [TP] (g/L) | 21.0 | 20.5 | 18.1 |
| **Heavy stream** | | | |
| $F_{HPROD}$ ($m^3/h$) | 0.166 | 0.187 | 0.187 |
| $M^M$ (g/L) | 7.71 | 13.2 | 33.3 |
| [TP] (g/L) | 101 | 105 | 161 |

Table 4

| | UF Configuration | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Basic | | | Linear | | | Dual | | |
| | NF Configurations | | | | | | | | |
| | Basic | Linear | Dual | Basic | Linear | Dual | Basic | Linear | Dual |
| $Y^M$ | 62.5 | 80.3 | 91.8 | 58.6 | 75.3 | 86.2 | 46.5 | 59.7 | 68.4 |
| $X^M$ | 49.3 | 42.0 | 33.1 | 49.5 | 41.6 | 32.5 | 47.3 | 39.1 | 29.9 |
| $X^L$ | 35.6 | 42.1 | 42.9 | 37.4 | 43.6 | 44.0 | 40.4 | 46.3 | 45.8 |
| $X^M / X^L$ | 1.39 | 1.00 | 0.77 | 1.32 | 0.95 | 0.74 | 1.17 | 0.84 | 0.65 |
| **Medium stream** | | | | | | | | | |
| $F_{MPROD}$ ($m^3$/h) | 0.169 | 0.190 | 0.221 | 0.169 | 0.190 | 0.221 | 0.169 | 0.190 | 0.221 |
| $M^M$ (g/L) | 75.9 | 86.7 | 85.2 | 71.2 | 81.4 | 80.1 | 56.4 | 64.5 | 63.5 |
| $M^L$ (g/L) | 54.8 | 86.9 | 110.5 | 53.9 | 85.4 | 108.7 | 48.2 | 76.4 | 97.2 |
| [TP] (g/L) | 154 | 207 | 257 | 144 | 196 | 247 | 119 | 165 | 212 |
| **Light stream** | | | | | | | | | |
| $F_{LPROD}$ ($m^3$/h) | 7.165 | 7.144 | 7.113 | 7.144 | 7.123 | 7.092 | 7.144 | 7.123 | 7.092 |
| $M^M$ (g/L) | 0.89 | 0.39 | 0.06 | 0.84 | 0.36 | 0.05 | 0.67 | 0.29 | 0.04 |
| [TP] (g/L) | 9.1 | 7.3 | 4.8 | 9.0 | 7.2 | 4.8 | 8.1 | 6.55 | 4.4 |

Table 5

| Costs | Total protein limit (g/L) | | | | | | |
|---|---|---|---|---|---|---|---|
| ($/d) | 100 | 125 | 150 | 175 | 200 | 225 | 250 |
| **TC** | 1173.5 | 1010.4 | 903.5 | 829.3 | 776.2 | 738.2 | 712.4 |
| **CC** | **187.1** | **166.4** | **154.2** | **147.6** | **145.1** | **146.3** | **151.5** |
| **$CC_{memb}$** | 74.9 | 66.9 | 62.3 | 60.0 | 59.4 | 60.5 | 63.6 |
| **$CC_{membUF}$** | 48.1 | 42.4 | 39.0 | 36.9 | 35.7 | 35.3 | 35.6 |
| **$CC_{membNF}$** | 26.8 | 24.5 | 23.3 | 23.1 | 23.7 | 25.2 | 28.0 |
| **$CC_{inst}$** | 112.2 | 99.5 | 91.9 | 87.6 | 85.7 | 85.8 | 87.9 |
| **$CC_{instUF}$** | 96.1 | 84.8 | 77.9 | 73.7 | 71.5 | 70.6 | 71.1 |
| **$CC_{instNF}$** | 16.1 | 14.7 | 14.0 | 13.9 | 14.2 | 15.1 | 16.8 |
| **OC** | **986.4** | **844.1** | **749.3** | **681.7** | **631.1** | **592.0** | **560.8** |
| **$OC_{en}$** | 11.3 | 9.1 | 7.7 | 6.6 | 5.9 | 5.2 | 4.8 |
| **$OC_{m}$** | 9.4 | 8.3 | 7.7 | 7.4 | 7.3 | 7.3 | 7.6 |
| **$OC_{lab}$** | 288.0 | 288.0 | 288.0 | 288.0 | 288.0 | 288.0 | 288.0 |
| **$OC_{clean}$** | 64.8 | 64.8 | 64.8 | 64.8 | 64.8 | 64.8 | 64.8 |
| **$OC_{water}$** | 613.0 | 473.9 | 381.2 | 315.0 | 265.3 | 226.7 | 195.7 |

Table 6

| Product stream characteristics | Total protein limit (g/L) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 100 | 125 | 150 | 175 | 200 | 225 | 250 |
| $F_{MPROD}$ ($m^3$/d) | 6.3 | 5.0 | 4.2 | 3.6 | 3.1 | 2.8 | 2.5 |
| $M^M$ (g/L) | 49.3 | 61.6 | 73.9 | 86.2 | 98.5 | 110.8 | 123.1 |
| Z ($/$m^3$) | 188 | 202 | 217 | 232 | 248 | 265 | 285 |

Table 7

| Costs ($/d) | Total protein limit (g/L) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 100 Min Water | 100 Min TC | 150 Min Water | 150 Min TC | 200 Min Water | 200 Min TC | 250 Min Water | 250 Min TC |
| **TC** | 596.0 | 596.0 | 549.6 | 549.6 | 534.0 | 533.8 | 537.2 | 531.3 |
| **CC** | **196.0** | **196.0** | **159.7** | **159.7** | **148.9** | **148.3** | **154.4** | **147.0** |
| **$CC_{memb}$** | 80.4 | 80.4 | 65.7 | 65.7 | 61.8 | 61.5 | 65.4 | 61.0 |
| **$CC_{membUF}$** | 48.1 | 48.1 | 39.0 | 39.0 | 35.7 | 35.7 | 35.6 | 35.3 |
| **$CC_{membNF}$** | 32.4 | 32.4 | 26.8 | 26.8 | 26.1 | 25.7 | 29.8 | 25.7 |
| **$CC_{inst}$** | 115.6 | 115.6 | 94.0 | 94.0 | 87.1 | 86.9 | 89 | 86.0 |
| **$CC_{instUF}$** | 96.1 | 96.1 | 77.9 | 77.9 | 71.5 | 71.5 | 71.1 | 70.6 |
| **$CC_{instNF}$** | 19.4 | 19.4 | 16.1 | 16.1 | 15.6 | 15.4 | 17.9 | 15.4 |
| **OC** | **400.0** | **400.0** | **389.8** | **389.8** | **385.1** | **385.5** | **382.8** | **384.4** |
| **$OC_{en}$** | 25.6 | 25.6 | 17.2 | 17.2 | 13.0 | 13.4 | 10.5 | 12.4 |
| **$OC_{m}$** | 9.8 | 9.8 | 8.0 | 8.0 | 7.4 | 7.4 | 7.7 | 7.4 |
| **$OC_{lab}$** | 288.0 | 288.0 | 288.0 | 288.0 | 288.0 | 288.0 | 288 | 288.0 |
| **$OC_{clean}$** | 76.6 | 76.6 | 76.6 | 76.6 | 76.6 | 76.6 | 76.6 | 76.6 |
| **$OC_{water}$** | - | - | - | - | - | - | - | - |

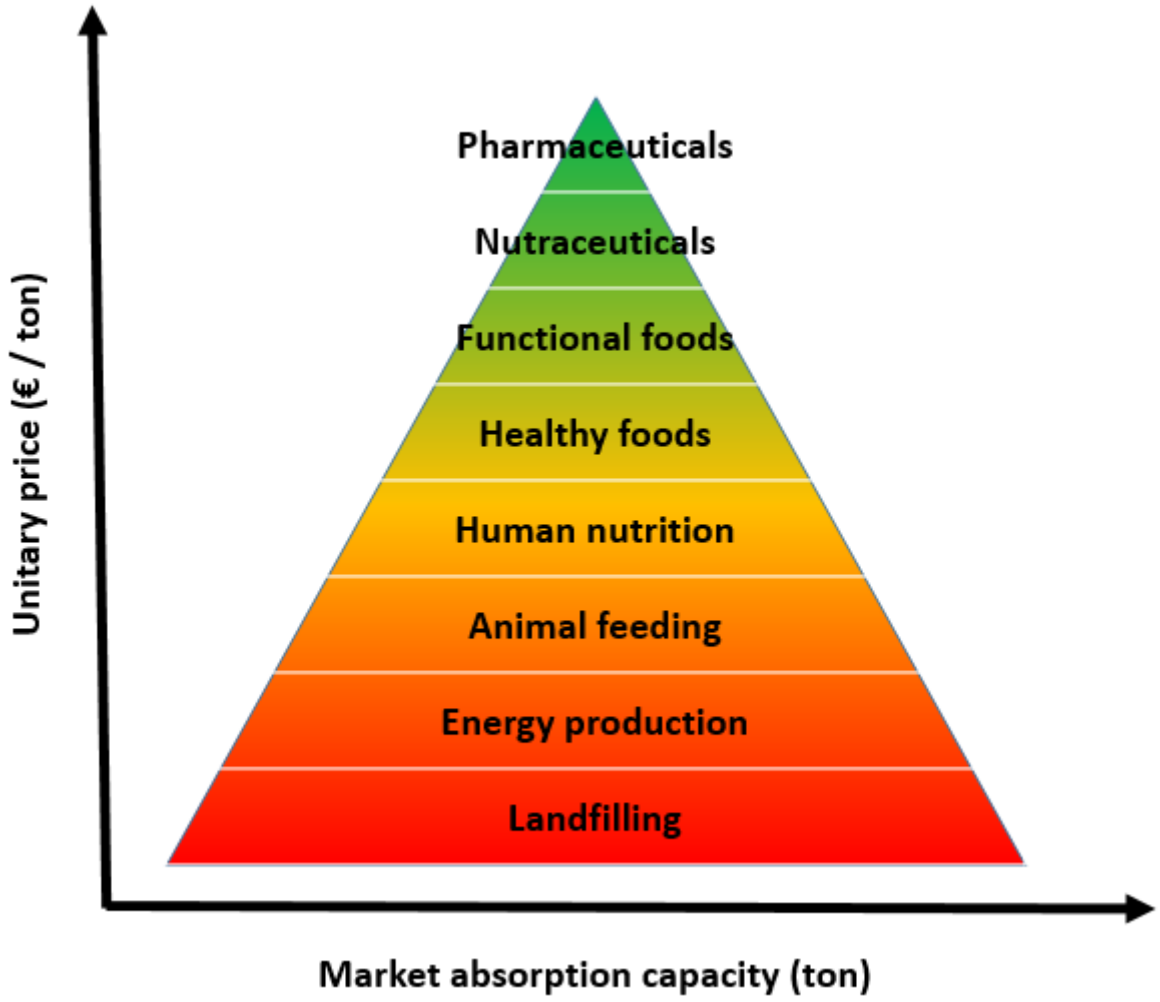



Figure 1

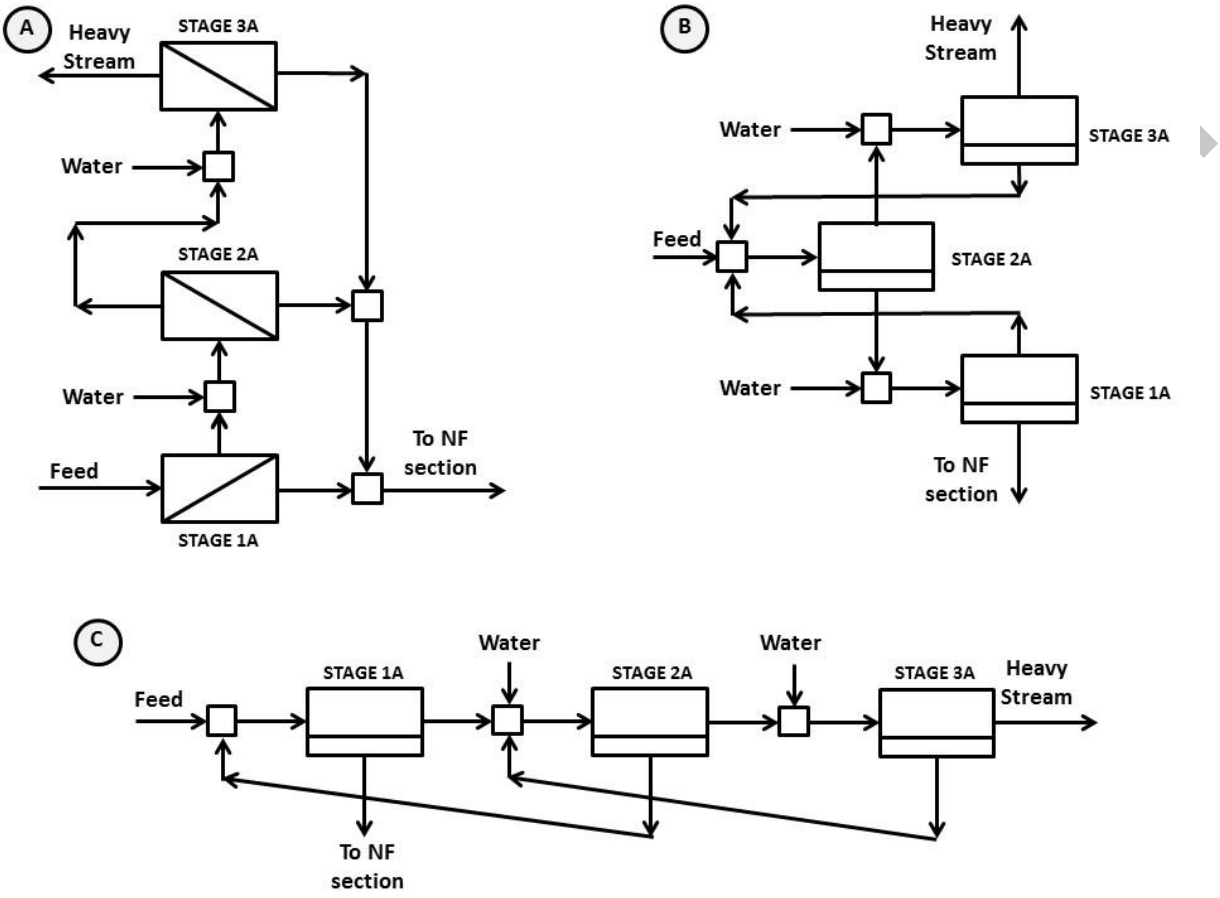



Figure 2

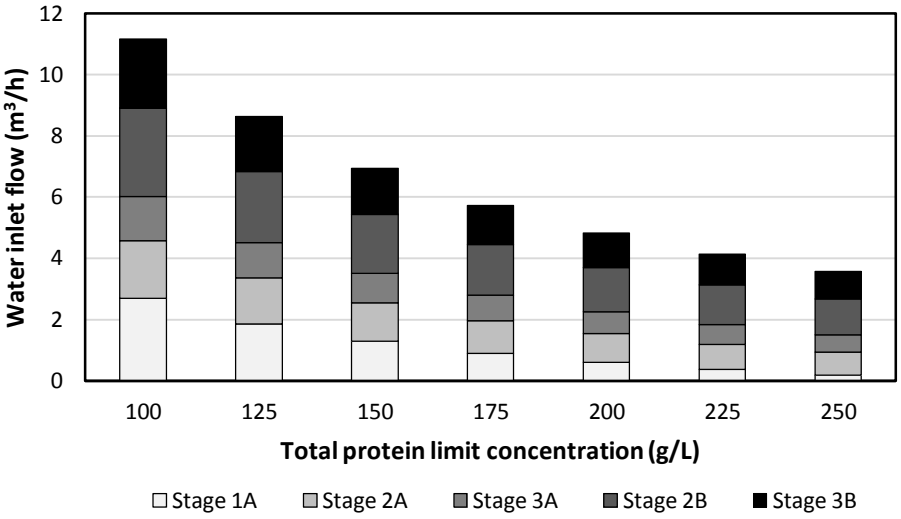
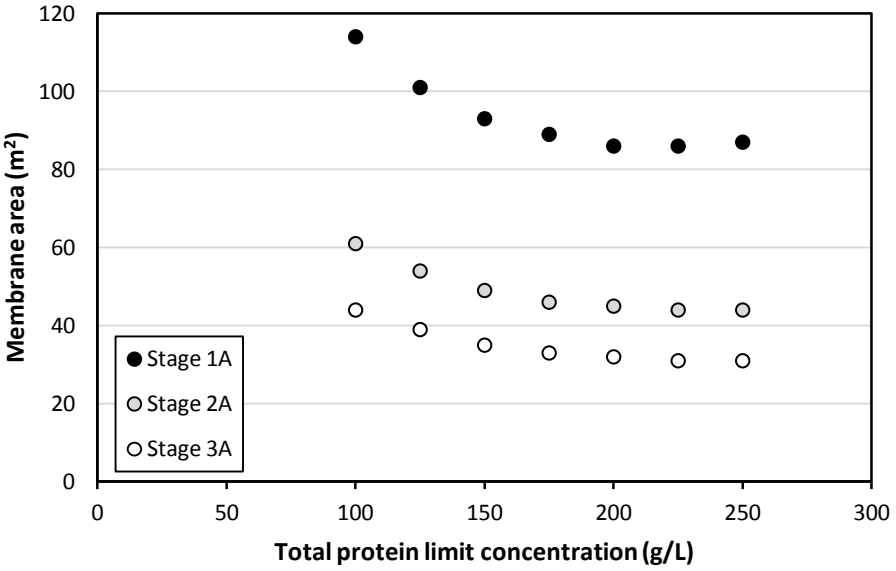



Figure 3

a)




b)

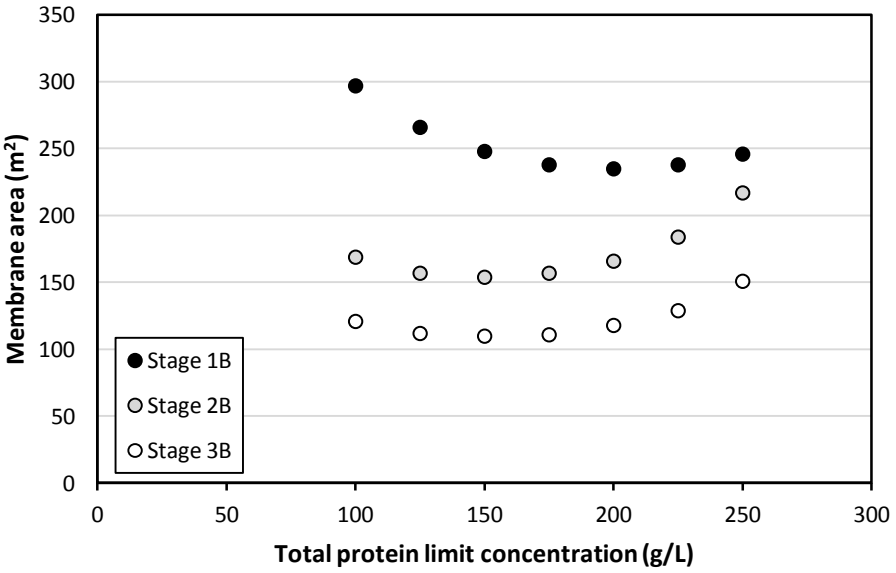



Figure 4

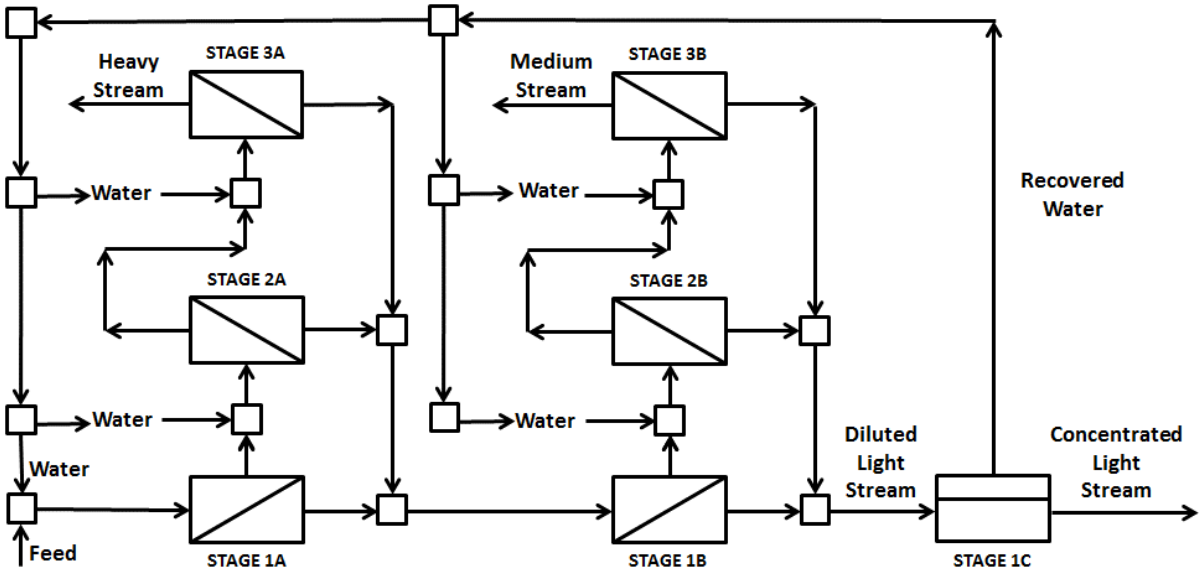



Figure 5

# OPTIMAL DESIGN OF INDUSTRIAL SCALE CONTINUOUS PROCESS FOR FRACTIONATION BY MEMBRANE TECHNOLOGIES OF PROTEIN HYDROLYSATE DERIVED FROM FISH WASTES

Supplementary information

## Equations of the model

### Mass balances (total, total protein content and by fractions)

Mixers

$$F_{IN1} + F_{IN2} = F_{OUT}$$

$$F_{IN1} \cdot [TP]_{IN1} + F_{IN2} \cdot [TP]_{IN2} = F_{OUT} \cdot [TP]_{OUT}$$

$$F_{IN1} \cdot M^{i}_{IN1} + F_{IN2} \cdot M^{i}_{IN2} = F_{OUT} \cdot M^{i}_{OUT}$$

Membrane modules

$$F_{UP} = F_{PERM} + F_{RET}$$

$$F_{UP} \cdot [TP]_{UP} = F_{PERM} \cdot [TP]_{PERM} + F_{RET} \cdot [TP]_{RET}$$

$$F_{UP} \cdot M^{i}_{UP} = F_{PERM} \cdot M^{i}_{PERM} + F_{RET} \cdot M^{i}_{RET}$$

### Membrane transport

$$F_{PERM} = A_{MEMB} \cdot J_P = A_{MEMB} \cdot \left[ L_{P0} - K_R \left( \frac{[TP]_{UP} + [TP]_{RET}}{2} \right)^{0.5} \right] \cdot \Delta P$$

$$M^{i}_{PERM} = M^{i}_{UP} \cdot (100 - R^{i})/100$$

| Peptide Fractions | Rejections $R^i$ (%) | |
|---|---|---|
| | UF Membrane | NF Membrane |
| **UH** | 100 | 100 |
| **H** | 96 - 7.75(ΔP) | 100 |
| **M** | 33 | $-0.42(\Delta P)^2 + 7.7(\Delta P) + 58$ |
| **L** | 21 | $-0.64(\Delta P)^2 + 13(\Delta P) + 15$ |
| **UL** | 16 | $-0.76(\Delta P)^2 + 16(\Delta P) - 28$ |

### Definition of parameters

$$Rec = \frac{F_{PERM}}{F_{UP}}$$

$$X^{M} = 100 \frac{M^{M}_{MPROD}}{[TP]_{MPROD}}$$

$$Y^{M} = 100 \frac{F_{MPROD} \cdot M^{M}_{MPROD}}{F_{FEED} \cdot M^{M}_{FEED}}$$

**Freshwater consumption**

$$F_{WATER} = \sum F_{Wk}$$

**Cost estimation**

$$TC = CC + OC$$

$$CC = CC_{memb} + CC_{inst}$$

$$CC_{memb} = CC_{membUF} + CC_{membNF}$$

$$CC_{membUF} = \frac{Y_{membUF} \sum A_{UFk}}{LT_{membUF}}$$

$$CC_{membNF} = \frac{Y_{membNF} \sum A_{NFk}}{LT_{membNF}}$$

$$CC_{inst} = CC_{instUF} + CC_{instNF}$$

$$CC_{instUF} = CC_{membUF} \frac{(1 - K_{memb})}{K_{memb}} \frac{LT_{membUF}}{LT_{inst}}$$

$$CC_{instNF} = CC_{membNF} \frac{(1 - K_{memb})}{K_{memb}} \frac{LT_{membNF}}{LT_{inst}}$$

$$OC = OC_{water} + OC_{en} + OC_{clean} + OC_{lab} + OC_{m}$$

$$OC_{water} = Y_{water} \sum Q_{water}$$

$$OC_{en} = \frac{\sum (F_{UPk} \Delta P_{k})}{36\eta} Y_{elec}$$

$$OC_{clean} = Y_{clean} \sum \left( F_{UPk} \frac{[TP]_{UPk}}{[TP]_{REF}} \right)$$

$$OC_{lab} = 24 n_{lab} Y_{lab}$$

$$OC_{m} = 0.05 CC$$

**Restrictions**

$$0.1 < Rec_i < 0.9$$

$$2 \text{ bar} < \Delta P_{UF} < 6 \text{ bar}$$

$$5 \text{ bar} < \Delta P_{NF} < 15 \text{ bar}$$

$$[TP]_{ST} < [TP]_{limit}$$

$$X^M > X^M{}_{limit}$$

$$Y^M > Y^M{}_{limit}$$

**Objectives**

Minimize $F_{WATER}$

Minimize TC